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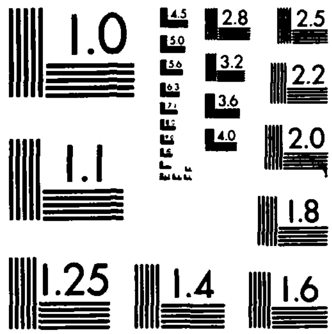

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by

Paul J. Hans and Bernard Gordon III

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WITTING SYNTHESIS OF CONDUCTIVE SEGMENTED BLOCK POLYMER COMPOSITIONS.
Conducting polymers such as polyacetylene and polyparaphenylene have been shown to have electrical conductivities which vary from the insulator to semiconductor and metallic regimes upon doping with electron acceptor or donor molecules. Unfortunately, many of these materials are plagued by undesirable properties such as oxidative instability (in the case of polyacetylene) and intractability or infusibility. Researchers have attempted improvements of the physical properties and environmental stability of polyacetylene by blending with elastomers, preparing composites with polyethylene film, and synthesizing block and graft copolymers. Some enhancements of the physical properties of the mate-ials (eg. mechanical behavior, solubility behavior) compared to polyacetylene were generally observed. Electrical conductivities were generally less than for pure polyacetylene although stretching blend films was observed to enhance the conductivity, often by an order of magnitude over the unstretched film. In this paper we reported

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on the preparation of segmented block polymers prepared via a Wittig condensation of conductive poly(p-phenylene pentadienylene) oligomers and linear alkanes. It is felt that preparation of segmented block polymers will result in conductive materials with good mechanical properties providing phase morphology and size can be controlled.

WITTIG SYNTHESIS OF CONDUCTIVE SEGMENTED BLOCK POLYMER COMPOSITIONS

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Conducting polymers such as polyacetylene and polyparaphenylene have been shown to have electrical conductivities which vary from the insulator to semiconductor and metallic regimes upon doping with electron acceptor or donor molecules, such as AsF_5 and Na respectively. Unfortunately these materials are plagued by undesirable properties such as oxidative instability (in the case of polyacetylene) and intractability or infusibility. Researchers have attempted improvements of the physical properties and environmental stability of polyacetylene by blending with elastomers [1-3, 13a, 13b], preparing composites with polyethylene film by insitu polymerizations [4,5, 13c], and synthesizing block [6,7] and graft [15] copolymers. Some enhancements of the physical properties of the materials (eg. mechanical behavior, solubility behavior) compared to polyacetylene were generally observed. Electrical conductivities were generally less than for pure polyacetylene although stretching blend films was observed to enhance the conductivity, often by an order of magnitude over the unstretched film [1, 13a].

Work in our laboratory has focused on an alternate route to n-type electrically conductive polymers, namely by proton abstraction doping (PAD) [8,9]. For example, it was shown [10,11] that Poly(p-phenylene pentadienylene), 1, could be prepared via a Wittig synthesis as shown in Figure 1.

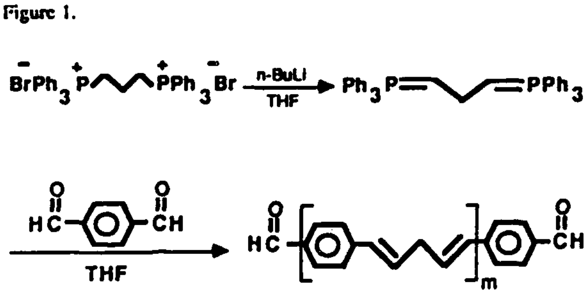

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Figure 1.

Here the conjugated backbone is interrupted by an isolated sp^3 hybridized methylene moiety per repeat unit. This should result in increased oxidative stability of the undoped material as well as increasing the overall flexibility of the backbone. Subjecting 1 to base (n-BuLi) was shown to result in abstraction of a doubly allylic methylene proton resulting in a charge delocalized system (carbanion) and observed conductivities on the order of 10^{-1} $(\Omega\text{-cm})^{-1}$.

While the inclusion of a methylene unit adds flexibility to the undoped material, doping to the carbanion form would result in sp^2 hybridization and hence a stiffer chain. It was, therefore, felt that chain extending the conductive poly(p-phenylene pentadienylene) segments with flexible groups would allow us to prepare conductive materials with good to excellent mechanical properties. We will report on the synthesis and characterization of segmented block polymers, structure 2, prepared via a Wittig route from oligomers of 1 and linear alkanes, as shown in Figure 2. The results of NMR and IR spectral analysis will be presented along with room temperature d.c. electrical conductivity data (as determined by direct resistance and four probe measurements).

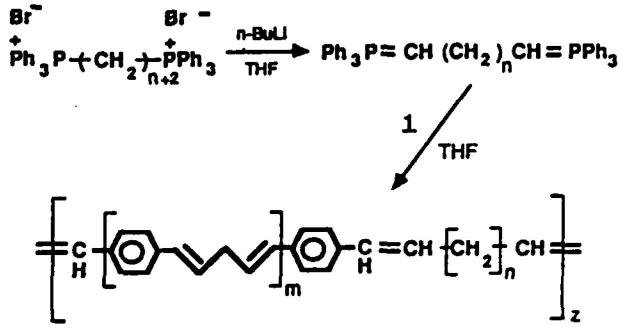

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Figure 2.

Two comments can be made about this approach. Gourley et al., [14] studying poly(p-phenylene vinylene) oligomers observed that the conductivities were not strongly affected by the degree of polymerization. This suggests that long conjugated chains are not necessary for conduction. Galvin and Wnek [4, 13c] observed an apparent percolation threshold of the electrical conductivity at approximately 3 weight % polyacetylene in the polyethylene film composites. Attempts at dispersing polyacetylene powder in polyethylene films cast from solution did not yield high conductivities (upon doping) even at loadings as high as 40 weight % polyacetylene. This was rationalized as being due to a "combination of particle size and wettability effects" [13c]. Transmission electron microscopy data of a composite sample indicated irregularly shaped dispersed phases of polyacetylene (on the order of 600 - 2000Å) in the polyethylene matrix. On the other hand, the films loaded with powdered polyacetylene were "grossly inhomogeneous on a macroscopic scale." [4] By varying the lengths of the conducting and soft segments we hope to be able to control the phase morphology and phase size in the block polymers obtaining microdomains of poly(p-phenylene pentadienylene) dispersed in the alkane matrix, analogous to conventional segmented block polymer systems [16].

The doped form of 1, being a carbanion, is highly reactive towards proton sources and oxygen and therefore would not be stable in an air environment. Current work in our laboratory is aimed at chemically stabilizing the delocalized carbanions [12]. The formation of segmented block polymers offers the possibility of physically stabilizing the conductive segments by surrounding them in a matrix of insulating segments in a manner somewhat analogous to work performed with polyacetylene [1,2,5].

Finally, we will present room temperature d.c. conductivity data on a series of low molecular weight delocalized carbanions of increasing length of conjugation. These are shown in Figure 3 along with some preliminary conductivity data for three of the anions measured by the direct resistance method. The anions were prepared using the Lochmann's base mixture [17] (equimolar amounts of potassium tert-butoxide and n-butyl lithium in pentane) as the metallating system. It should be noted that the linear heptatrienyl anion readily cyclizes to the cycloheptatrienyl anion [18] above -30°C and therefore could not be measured. The salts were washed thoroughly with dry pentane, dried under vacuum (< 0.01 mm Hg) and the electrical conductivity was measured using the direct resistance and four probe methods.

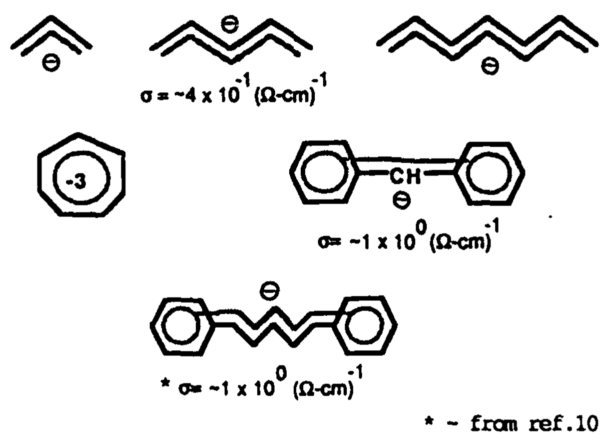

Figure 3

In summary, segmented block polymers have been prepared via a Wittig condensation of poly(p-Phenylene pentadienylene) oligomers and linear alkanes and their conductivities measured. It is felt that preparation of segmented block polymers will result in conductive materials with good mechanical properties providing phase morphology and size can be controlled. In addition, the conductivities of a series of low molecular weight delocalized carbanions have been reported.

Acknowledgements

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